
PREFACE

Among the available renewable energy resources fuel cell is an emerging area for the production of electricity. The major drive to use fuel cells in place of conventional power systems is their efficiency, reliability, modularity, fuel flexibility, and environmental friendliness. There are so many types of fuel cells which are categorized based on the kind of electrolyte they employ. Among them, solid oxide fuel cells (SOFCs) have many advantages over others. SOFCs are clean and highly efficient energy conversion electrochemical devices. SOFCs have three main components namely an anode, an electrolyte and a cathode. The electrolyte plays a major role through which oxygen ions migrate constituting electric current. These should have high ionic conductivity, negligible electronic conductivity and very little porosity to avoid the crossover of the gases, stability in oxidizing and reducing atmosphere, thermally compatible with the anode and cathode and low cost. The present thesis is divided into nine chapters:

Chapter 1: Introduction and literature review

This chapter focuses on the some basic concepts of fuel cells and their classifications and an overview of the literature on the solid electrolytes; viz YSZ, bismuth oxide, lanthanum gallate, doped and co-doped ceria and ceria/salt based nanocomposites. At present SOFCs employ yttria stabilized zirconia, (YSZ) as the solid electrolyte. YSZ shows high oxide ion conductivity at high temperature ~ 1000 °C and desired stability in both the oxidizing and reducing atmosphere. But high operating temperature of YSZ has a large number of engineering and material problems. Many efforts have been made to reduce the operating temperature of SOFCs (500-700 °C) using different type of electrolytes called intermediate temperatures SOFCs (IT-SOFCs). IT-SOFCs removes all the problems associated with the high working temperature of YSZ based fuel cells.

Similar to zirconia ceria also has fluorite structure and it has good compatibility with the electrodes. Ceria doped with aliovalent cations has high ionic conductivity particularly at low temperature as compared to zirconia. The main compensating

defect in ceria is the oxygen vacancies. Samarium, $\text{Ce}_{0.80}\text{Sm}_{0.20}\text{O}_{1.90}$ (SDC) and gadolinium, $\text{Ce}_{0.80}\text{Gd}_{0.20}\text{O}_{1.90}$ (GDC) doped ceria have been found to have the highest ionic conductivity for IT-SOFC. SDC and GDC show ionic conductivity 0.1 S/cm at 700 °C. But, Gd and Sm are very costly. The main disadvantages of SDC and GDC are that they possess electronic conduction at higher temperature due to conversion of Ce^{4+} to Ce^{3+} . A co-doping approach has been found to further enhance the ionic conductivity of doped ceria in the intermediate temperature range and it also reduces the electronic conduction.

At present, work has been going on ceria/carbonate based nanocomposites to further reduce the working temperature of ceria based solid electrolytes in the range 300-600 °C. Composite electrolytes contain two phases, one based on crystalline ceria oxide and the other is of an amorphous salt. It has been observed that the interfaces formed between the two phases provide more conducting channels for the transport of the ions. Electric field distribution in the interfaces between the two phases is a key to realize the interface ionic conduction in addition to the bulk conduction. This causes a sudden increase in the conductivity at a certain temperature called superionic transition temperature.

Chapter 2: Objective of the present work

In the present work, in order to reduce the cost, rare earth ions have been replaced partly by the alkaline earth ions. To increase the grains, grain boundaries as well as the total conductivity in the intermediate temperature range (500-700 °C), some singly and co-doped (containing at least one alkaline earth ion) ceria solid electrolytes have been prepared and characterized.

Nanocomposites of these samples have been prepared to further enhance the conductivity of co-doped ceria based electrolytes at low temperatures (300-600 °C). The compositions which have the highest total ionic conductivity in the series of compounds investigated have been chosen for the nanocomposites. The samples have been synthesized using citrate-nitrate gel auto-combustion route and characterized for thermal behavior, phase, crystal structure, microstructure, elemental analysis and electrical conductivity.

Chapter 3: Experimental work

This chapter deals with the experimental techniques: (i) All the doped and the co-doped ceria samples are prepared using citrate nitrate auto-combustion route. (ii) Nanocomposites have been prepared by mixing nanocrystalline ceria powders with the binary mixture of Li_2CO_3 and Na_2CO_3 . (iii) Thermal behavior of all the samples is studied using DTA/TGA. (iv) Phases, crystal structure, morphology, elemental analysis and coefficient of thermal expansion have been studied using XRD, SEM, EDS and dilatometer respectively. (v) Electrical conductivity has been studied employing complex plane impedance analysis.

Chapter 4: La and Sr co-doped ceria, $\text{Ce}_{1-x-y}\text{La}_x\text{Sr}_y\text{O}_{2-\delta}$ (fixed oxygen vacancies) and its nanocomposites

This chapter deals with the synthesis and characterization of compositions in the system $\text{Ce}_{1-x-y}\text{La}_x\text{Sr}_y\text{O}_{2-\delta}$. In this system total number of oxygen vacancies is kept constant to study the effect of co-doping with La^{3+} and Sr^{2+} . Single phase formation has been found in all the samples. More than 94% of the theoretical density has been observed in all the samples. An improvement in the grains, grain boundaries as well as the total conductivity has been found by partial substitution of La^{3+} by Sr^{2+} in ceria. Sr^{2+} has been found to be a good grain boundaries scavenger. The composition $\text{Ce}_{0.89}\text{La}_{0.07}\text{Sr}_{0.04}\text{O}_{1.90}$ shows the highest conductivity in this system. It is higher than that reported for SDC and GDC. Use of this composition as solid electrolyte for IT-SOFCs will reduce the cost subject to their thermodynamic stability and compatibility with other components of the cell.

Nanocomposites of $\text{Ce}_{0.89}\text{La}_{0.07}\text{Sr}_{0.04}\text{O}_{1.925}$ (CL7S4) have been prepared and characterized. Single phase formation has been found in all the composite samples. The carbonates are present as an amorphous phase in the composites. The composition containing 35 wt% of the carbonates shows the maximum conductivity. Its value is two orders of magnitude higher than that of CL7S4. Enhancement in the conductivity is attributed to a superionic transition at the interfaces formed between the two phases.

Chapter 5: La and Sr co-doped ceria, $\text{Ce}_{0.85}\text{La}_{0.15-x}\text{Sr}_x\text{O}_{2-\delta}$ (changed oxygen vacancies) and its nanocomposites

This chapter deals with the synthesis and characterization of compositions in the system $\text{Ce}_{0.85}\text{La}_{0.15-x}\text{Sr}_x\text{O}_{2-\delta}$. In this system total number of oxygen vacancies is changed with increasing the concentration of Sr. All the samples have density more than 95% of the theoretical value. Conductivity of the co-doped samples is higher than that of singly La doped ceria. Bulk conductivity increases with increasing Sr content up to 2.5 mol% and decreases at higher concentration of Sr. Conductivity of the grain boundaries strongly depends on the average grain size of the samples. The composition with $x=0.025$ shows the maximum conductivity. Its value is more than the values reported for SDC and GDC.

Nanocomposites of $\text{Ce}_{0.85}\text{La}_{0.125}\text{Sr}_{0.025}\text{O}_{1.9125}$ (CL125S025) have been prepared by mixing CL125S025 nanocrystalline powder with different amount of $(\text{Li-Na})_2\text{CO}_3$. All the composite samples have fluorite structure similar to ceria. There is no peak of the carbonate phase in the XRD patterns. This confirms that the carbonate phase is present as an amorphous phase. A jump in the conductivity plots has been found in the composite samples at a particular temperature. This is ascribed to a superionic transition at the interfaces due to interfacial interaction. The composition with 35 wt% of the carbonate phase shows the maximum conductivity. Its value is much more than that of the $\text{Ce}_{0.85}\text{La}_{0.125}\text{Sr}_{0.025}\text{O}_{1.9125}$. At 475 °C, it has a value of 0.186 S/cm which is one order of magnitude more than 0.01 S/cm observed in $\text{Ce}_{0.8}\text{Sm}_{0.1}\text{Nd}_{0.1}\text{O}_{1.9}/(\text{Li/Na})_2\text{CO}_3$ by Liu et al. at 481 °C. Use of this electrolyte for LT-SOFCs will reduce the cost subject to their thermodynamic stability and compatibility with other components of the cell.

Chapter 6: Sm and Sr co-doped ceria and its nanocomposites

This chapter describes the synthesis and characterization of Sm^{3+} and Sr^{2+} co-doped ceria solid electrolytes in the system, $\text{Ce}_{1-x-y}\text{Sm}_x\text{Sr}_y\text{O}_{2-\delta}$. In this system, the total number of oxygen vacancies has been kept constant to study the effect of co-doping of Sm^{3+} and Sr^{2+} . All the samples have been found to be single phase having density more than 95% of the theoretical density. SEM micrographs show a dense morphology with

varying grain size. The conductivity of the grains and the grain boundaries increases with increasing Sr content up to 2 mol% and then decreases at higher concentration of Sr. Samples 2SrSDC shows the maximum ionic conductivity 2.67×10^{-2} S/cm at 600 °C having minimum activation energy of conduction.

The composition, 2SrSDC (SSDC) has been chosen to prepare the nanocomposites. All the composite samples have fluorite structure similar to ceria. No peak of the carbonates is observed in the powder XRD patterns. A jump in the conductivity plots has been found in the composite samples. This corresponds to a superionic transition at the interfaces. The composite containing 35 wt% of the carbonate shows the maximum conductivity. Its value is one order of magnitude higher than that of SSDC. At 475 °C, SSDC/35 LNCO shows conductivity of 6.80×10^{-2} S/cm with an activation energy of conduction 0.48 eV.

Chapter 7: Ca and Sr co-doped ceria and its nanocomposites

This chapter deals with the synthesis and characterization of Ca^{2+} and Sr^{2+} co-doped ceria solid electrolytes for IT-SOFCs in the system, $\text{Ce}_{0.95-x}\text{Ca}_{0.05}\text{Sr}_x\text{O}_{2-\delta}$. All the compositions have been found to be single phase. All the samples have more than 97% of theoretical density. The samples co-doped with Ca and Sr exhibit higher ionic conductivity than the singly doped with Ca in the intermediate temperature range. The composition CC5S2 exhibits the maximum conductivity of all the compositions. Its conductivity at 600 °C (1.66×10^{-2} S/cm) is higher than the reported values of conductivity for SDC and GDC. Use of this electrolyte for IT-SOFCs will reduce the cost in comparison to SDC and GDC subject to their thermodynamic stability and compatibility with other components of the cell.

Nanocomposites of CC5S2 have been prepared by mixing CC5S2 with different wt% of binary mixture of Li_2CO_3 and Na_2CO_3 . In the composites, carbonates are present in the amorphous state. Crystalline ceria based single phase formation has been found in all the composites. A sudden increase in the conductivity has been observed in all the composites. Conductivity of the composites increases with increasing carbonate content due to increase in the interfacial area. The value of conductivity for the

composition, CC5S2/35LNCO is 0.27 S/cm at 500 °C and the activation energy of conduction in the temperature range 350-650 °C is 0.30 eV.

Chapter 8: Mg and Sr co-doped ceria and its nanocomposites

This chapter deals with the synthesis and characterization of Mg²⁺ and Sr²⁺ co-doped ceria solid electrolytes for IT-SOFCs. A few compositions in the system, Ce_{0.90}Mg_{0.10-x}Sr_xO_{1.90} keeping the total number of oxygen vacancies fixed have been prepared via citrate-nitrate route. Single phase formation has been observed in all the samples. More than 96% of theoretical density has been found in the samples. An improvement in the grains as well as grain boundaries conductivity has been found by partial substitution of Mg²⁺ by Sr²⁺ in the Ce_{0.90}Mg_{0.10}O_{1.90}. Scavenging effect of Sr in Mg-doped ceria has an advantageous effect on the overall conductivity because it can inhibit the formation of a continuous and uniform silicate phase along the grain boundaries. Ce_{0.90}Mg_{0.06}Sr_{0.04}O_{1.90} (CM6S4) shows the highest conductivity of all the compositions. Its use as a solid electrolyte for IT-SOFCs will reduce the cost as compared to using rare earth subject to their thermodynamic stability and compatibility with other components of the cell.

Composition, CM6S4 has been chosen to prepare the nanocomposites. All the composite samples have cubic fluorite structure similar to ceria. SEM images show that CM6S4 grains are fully covered by the amorphous carbonate phase. A superionic phase transition has been observed in all the composites. The composition, CM6S4/35LNCO shows the maximum conductivity, 0.4 S/cm at 500 °C with an activation energy 0.23 eV of conduction. This is two orders of magnitude more than that of CM6S4 (2.4×10^{-3} S/cm).

Chapter 9 Conclusion and future scope of the work

This chapter is an overview of the conclusions drawn from the present work. Scope of the future work is also proposed in this chapter.

- All the samples of singly doped, co-doped ceria and ceria/carbonate nanocomposites successfully prepared by citrate nitrate auto-combustion processing route show single phase formation having fluorite structure similar to ceria.

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- Single phase samples have density more than 93% and composite samples have density in the range 82-85% of the theoretical value.
 - SEM micrographs of single phase samples show a dense morphology with distinct grain and grain boundaries. In the composite samples, ceria grains are fully covered by the molten carbonate phase and the average grain size is about 100 nm.
 - EDS spectrum of the doped ceria samples show the presence of SiO₂ at the grain boundary whereas in Sr co-doped samples SiO₂ is scavenged off and segregates at the triple point junction.
 - Composition, Ce_{0.82}Sm_{0.16}Sr_{0.02}O_{1.90} shows the highest conductivity among all the samples investigated. Its value is higher than that of SDC and GDC.
 - Compositions with same number of oxygen vacancies follow the criteria of configurational entropy.
 - A jump in the conductivity plots has been observed in all the composite samples. This is due to superionic transition at the interfaces due to interfacial interaction.
 - Coefficient of thermal expansion of the composite samples has been found to be of the order of 10⁻⁶ /K in the temperature range 303-923 K.
 - Conductivity of composites is more above the transition temperature and less below the transition temperature than that of single phase ceria based electrolytes.
 - Conductivity of the composite electrolytes has been found to be of the order of 10⁻² -10⁻¹ S/cm. This may make these electrolytes as a potential candidate for LT-SOFCs as their use will reduce the cost subject to their thermodynamic stability and compatibility with other components of the cell.

Future scope of the work

- HR-TEM equipped with EELS and STEM analysis of these samples will be useful to know the exact composition of the silicate phases at the triple points.
- Conductivity measurement in H₂ atmosphere is important to confirm the multi-ion conduction in the composites.
- Single cell study of these samples will be useful to confirm their suitability for their potential use as solid electrolytes in IT-SOFCs and LT-SOFCs.